



An environmentally friendly triphasic catalytic system: Mn(salen) occluded in membranes based on PDMS/PVA

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ABSTRACT

The commercially available Jacobsen catalyst, Mn(salen), was occluded in hybrid polymeric membranes based on poly(dimethylsiloxane) (PDMS) and poly(vinyl alcohol) (PVA). The obtained systems were characterized by UV–vis spectroscopy and SEM techniques. The membranes were used as a catalytic barrier between two different phases: an organic substrate phase (cyclooctene or styrene) in the absence of solvent, and an aqueous solution of either t-BuOOH or H₂O₂. Membranes containing different percentages of PVA were prepared, in order to modulate their hydrophilic/hydrophobic swelling properties. The occluded complex proved to be an efficient catalyst for the oxidation of alkenes. The new triphasic system containing a cheap and easily available catalyst allowed substrate oxidation and easy product separation using “green” oxidants.

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1. Introduction

The production of bulk commodity chemicals from petroleum feedstocks often involves the use of a homogeneous catalyst, inorganic oxidants, and an organic solvent. In industrial organic syntheses there is a current trend toward the use of heterogeneous systems combined with clean oxidants such as H₂O₂ as environmentally friendly alternatives to the traditional oxidation reactions employing stoichiometric amounts of inorganic oxidants [1–8]. Elimination of organic solvents from the systems is also mandatory, since they are usually toxic and reduce reaction rates due to dilution.

Manganese complexes based on Schiff's base are known to be active homogeneous catalysts for epoxidation reactions in the presence of a variety of oxidants [9–20]. In some cases, their immobilization on solid matrices yields enhanced activity, increased stability, and easy recovery. Therefore, a variety of materials, such as clays [21,22], silica [23,24], and zeolites [25–30], have been investigated as supports for these complexes. Immobilization of Mn(salen) complexes on polymeric membranes has also received considerable attention [31–37]. The latter materials offer several advantages concerning their affinity for reagents, which is the main property of polymers. The membrane controls the access of both

the substrate and the oxidant to the active site and improves the contact between the reactants and the catalyst. Additionally, the catalyst–membrane system confers shape-selectivity to the oxidation reactions, not to mention that the polymer isolates the catalytic complex, avoiding catalyst inactivation by aggregation or self-oxidative destruction [38–42]. However, one of the major drawbacks related to these systems is catalyst leaching from the membrane when the metallic complex exhibits affinity for the solvent. Fortunately, leaching problems can be solved (or minimized) in the absence of solvents [40].

Membranes based on poly(dimethylsiloxane) (PDMS) exhibit good thermal, mechanical, and chemical stabilities. Furthermore, this polymer presents flexible siloxane chains, which provide fast mass transfer through the membrane and creates a hydrophobic environment around the metal active site, thus leading to reactant sorption control by means of preferential uptake of apolar molecules such as alkanes and alkenes [38–42]. PDMS-based membranes have been earlier used for the immobilization of metalloporphyrins [43], metallophthalocyanines [44], rhodium complexes [45], and Mn(salen) complexes [31–33]. These membranes can also be employed in order to maintain the two liquid reagent phases apart, thereby completely eliminating the need for a solvent or phase-transfer agents.

In a previous work [31], we used hybrid polymeric membranes based on poly(dimethylsiloxane) (PDMS) as supports for the occlusion of Jacobsen catalyst. The resulting system was used as a catalytic barrier between an aqueous solution of either t-BuOOH

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or H_2O_2 and an organic substrate phase (cyclohexane, cyclooctene, cyclohexene, or styrene). The occluded complex proved to be an efficient catalyst for the oxidation of alkanes and alkenes when $t\text{-BuOOH}$ was used as oxidant. However, H_2O_2 was not active in this catalytic system because the hydrophobic membrane created a barrier against this oxidant, preventing its sorption and, consequently, oxidation of organic substrates.

As a result of increased environmental concerns, the development of efficient oxidation catalysts and clean catalytic processes has been the subject of intensive research [1,5,46–50]. In this context, the design of polar membranes with a high degree of swelling for the “green” oxidant (H_2O_2) is necessary. An approach to obtaining these more polar membranes consists in combining polymers with different polarities. Recently, we have described the synthesis of semi-interpenetrating networks based on poly(dimethylsiloxane) (PDMS) and poly(vinyl alcohol) (PVA), in order to modulate the high hydrophobic character of the PDMS-based membrane and to achieve an adequate hydrophilic/hydrophobic balance [51]. Such desired feature was obtained thanks to the presence of hydrophilic ($-\text{OH}$) and hydrophobic ($\text{Si}-(\text{CH}_3)_2$) moieties. There was an enhancement in the hydrophilic character of these so-called PDMS/PVA semi-IPNs with increasing PVA amount, thereby leading to high equilibrium contents with polar solvents, including water, without loss of the membrane's ability to swell less polar solvents. These features make these PDMS/PVA semi-IPNs membranes potentially applicable in heterogeneous catalysis using hydrogen peroxide as oxidant, as will be demonstrated in this paper.

In this work we present the development of a reactor system involving the Jacobsen catalyst encapsulated in a membrane based on PDMS/PVA semi-IPNs that can selectively permeate hydrogen peroxide, in addition to organic substrates. This membrane was used as a catalytic barrier between an aqueous solution of the oxidant and an organic substrate phase (cyclooctene or styrene). Membranes containing different percentages of PVA were prepared, in order to modulate the hydrophilic/hydrophobic properties of the barrier.

2. Experimental

2.1. Materials

Jacobsen catalyst was purchased from Acros Organics and used as received. Alkenes (Z-cyclooctene and styrene) were purified in a short activated alumina column (Merck) immediately before use. Commercially available silanol-terminated poly(dimethylsiloxane) (PDMS) with a numeric average molecular weight of 2200 g/mol and tetraethoxysilane (TEOS) were supplied by Dow Corning. Poly(vinyl alcohol) with a degree of hydrolysis of 99 wt.% AS was purchased from Sigma–Aldrich. The di-n-butyltin–dilaurate complex 5 wt.% in hexane (Sn-catalyst) was purchased from Gelest. 2-Propanol (99.7% purity) was obtained from Grupo Química. Tert-butyl hydroperoxide ($t\text{-BuOOH}$, 70% solution in water) was acquired from Acros Organics, and hydrogen peroxide (30%) was obtained from Fluka.

2.2. Preparation of Jacobsen catalyst occluded in the polymeric membrane

Free polymeric membranes based on PDMS/PVA semi-IPNs as well as polymeric membranes containing encapsulated Jacobsen catalyst ($\text{Mn}(\text{salen})\text{PDMS/PVA}$) were obtained following the procedure described in Ref. [51]. In a typical synthesis, a proper amount of PVA (to give a composition of 10, 15, and 20 wt.% of PVA in the final membrane, considering that complete hydroly-

sis/condensation reactions between PDMS and TEOS took place) was dissolved in warm hot water, to give a 5 wt.% aqueous solution. A fixed amount of PDMS and TEOS was mixed with 2-propanol (10 mL), at room temperature, in the presence of the Sn-catalyst (less than 1 wt.%). This mixture was added to the PVA aqueous solution and, after complete mixing, heated to $\sim 85^\circ\text{C}$ for 7 h. After that, a volume of the Jacobsen catalyst solution ($1.51 \times 10^{-3} \text{ mol L}^{-1}$) in methanol, enough to provide 0.02% of this catalyst in relation to the total mass of the polymeric membrane, was added to this mixture. Viscous solutions were obtained, and they were cast onto Teflon™ Petri dishes and allowed to stand for ~ 15 days, at room temperature. The resulting films were then submitted to an isothermal treatment in an oven at 40°C , for 48 h. The resulting samples were labeled PDMS/PVA (the catalyst-free polymeric membrane), and $\text{Mn}(\text{salen})\text{PDMS/PVA}$ 1, 2, or 3 with 10, 15, or 20% PVA, respectively (all membranes contained 0.02 wt.% Jacobsen catalyst).

2.3. Sorption measurements

For the sorption measurements, dried sheet-shaped $\text{Mn}(\text{salen})\text{PDMS/PVA}$ samples were immersed in the substrate (cyclooctene or styrene) and oxidants ($t\text{-BuOOH}$ or H_2O_2), at 25°C . Membrane swelling was monitored until the film had reached a constant weight. Samples were withdrawn from the solvent every now and then, and weighed after removal of the surface solvent by light blotting with a filter paper. The sorption of alkenes and oxidants on the membrane was obtained by determining their swelling using the following expression [33,52].

$$\text{sorption}(\text{mmol g}^{-1}) = \frac{\{(W1 - W2)/W1\} \times 1000}{\text{MW}},$$

where $W1$ and $W2$ stand for the membranes weights (g) in the wet and dry states, respectively, and MW is the molecular weight of the alkene and oxidants.

The supernatant was analyzed by UV–vis spectroscopy, in order to check whether the Jacobsen catalyst had been leached from the membrane during the sorption experiments.

2.4. Characterization of $\text{Mn}(\text{salen})\text{PDMS/PVA}$ membrane

The electronic spectra of the $\text{Mn}(\text{salen})\text{PDMS/PVA}$ membranes containing occluded $\text{Mn}(\text{salen})$ were registered by maintaining the sample in the optical pathway of a UV–vis Hewlett-Packard 8452 diode array spectrometer, using the free polymer as reference. The spectra of the Jacobsen catalyst in solution were recorded in 10 mm path length quartz cell (Hellma). The morphology of the membranes was analyzed by scanning electron microscopy (SEM), using a JEOL-JSM-6360 LV microscope operating at 20 kV. The observed surface was obtained by coating the cryogenic fracture with a thin gold layer.

2.5. Oxidation reactions

The oxidation reactions were performed in the presence of the polymeric membrane (50 mg, containing $1.6 \times 10^{-8} \text{ mol}$ of the Jacobsen catalyst), which was used as a catalytic barrier between the aqueous phase containing the oxidant ($t\text{-BuOOH}$ or H_2O_2 ; $7.8 \times 10^{-4} \text{ mol}$), and the organic substrate phase (cyclooctene or styrene; $6.5 \times 10^{-3} \text{ mol}$), in a glass reactor specially designed for this study (Fig. 1). All reactions were carried out at room temperature using orbital stirring. The membrane was removed after 24 h, and the organic and aqueous phases were separated. The former phase was diluted with dichloromethane (0.75 mL), and the latter with methanol (0.75 mL). An internal standard (bromobenzene) was added to each phase, and the products were analyzed by gas chromatography on a Varian Star 3400 CX chromatograph

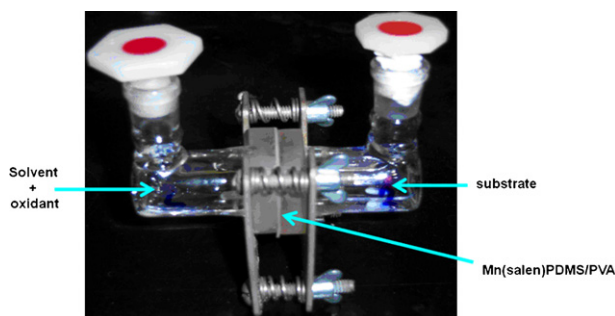


Fig. 1. Picture of the glass reactor used in this work. It was designed to support the catalytic polymeric membrane as a barrier between the aqueous phase (containing the oxidant) and the organic substrate.

equipped with an ionization flame detector. A DB-wax (1 mm thickness) megabore column (30 m \times 0.538 mm) was employed; nitrogen was used as the carrier gas. The results were recorded and processed on a Varian Workstation. Each reaction was carried out at least in triplicate. Control reactions were accomplished under the same conditions as those employed for the PDMS/PVA membrane.

3. Results and discussion

3.1. Characterization of the Mn(salen)PDMS/PVA membrane

The polymeric membranes based on PDMS/PVA semi-IPNs were synthesized by crosslinking silanol-terminated PDMS with TEOS in the presence of a Sn-catalyst, with the concomitant addition of a PVA solution. TEOS and silanol-terminated PDMS can react practically with all reactive functional groups, namely the four Si–OEt groups in TEOS and the two Si–OH groups in PDMS, with formation of ethanol as by-product, on the basis of hydrolysis/condensation reactions. The PVA chains are not crosslinked during this process. The resulting material is called semi-interpenetrating network (semi-IPN), since the PDMS are crosslinked by TEOS whereas the PVA chains are linear, thereby leading to dense polymeric materials.

In this work, we have prepared the different membrane compositions by varying the amount of free PVA in the PDMS network. The polymeric membranes displayed good thermal stability up to 250 °C, according to the thermogravimetric characterization (not shown here) [51]. In all cases, the Mn(salen) catalyst was the last compound to be added to the mixture. In Fig. 2 there is a schematic representation of the catalytic polymeric membrane, Mn(salen)PDMS/PVA.

The UV–vis spectra of the membranes Mn(salen)PDMS/PVA 1, 2, and 3 display the typical Mn(salen) bands at 255, 325, and 422 nm (Fig. 3). The band at 255 nm is assigned to the $\pi \rightarrow \pi^*$ transition of the benzene ring of salicylaldehyde, the band at 325 nm is attributed to the $n \rightarrow \pi^*$ transition of the azomethine chromophore, and the band at 422 nm is due to the $d \rightarrow d$ transition [53]. In homogeneous media, this complex displays bands at 244, 326, and 440 nm. Since the complex in homogeneous solution and the complexes immobilized on the membrane have similar UV–vis spectral profiles, it can be assumed that: (i) encapsulation in the hybrid polymeric membrane PDMS/PVA does not lead to any structural disturbance of the Jacobsen complex; and (ii) there are no electronic interactions between the central metal ion and the surrounding polymer in the case of the immobilized catalyst. Similar results have been described by other researchers for encapsulated catalysts based on Mn(salen) [54,55].

UV–vis spectra registered before and after the catalytic reaction did not reveal any difference in the spectral profile and absorbance of the fresh catalyst and the catalyst recovered after the oxidation reaction. This is a clear indication that the Jacobsen catalyst did not leach from the polymeric membrane. The increase in absorbance in the UV–vis spectra of Mn(salen)PDMS/PVA membranes 1–3 is due to the increasing opacity of the polymeric membranes, a consequence of the larger amount of PVA. So, although the amount of Jacobsen catalyst in all membranes is the same (0.02 wt.%), the increasing opacity of the membranes gives rise to higher absorbance values.

The surface cryogenic fractures of the studied membranes obtained in the presence and in the absence of the complex present similar homogeneous patterns, as can be seen in Fig. 4 for

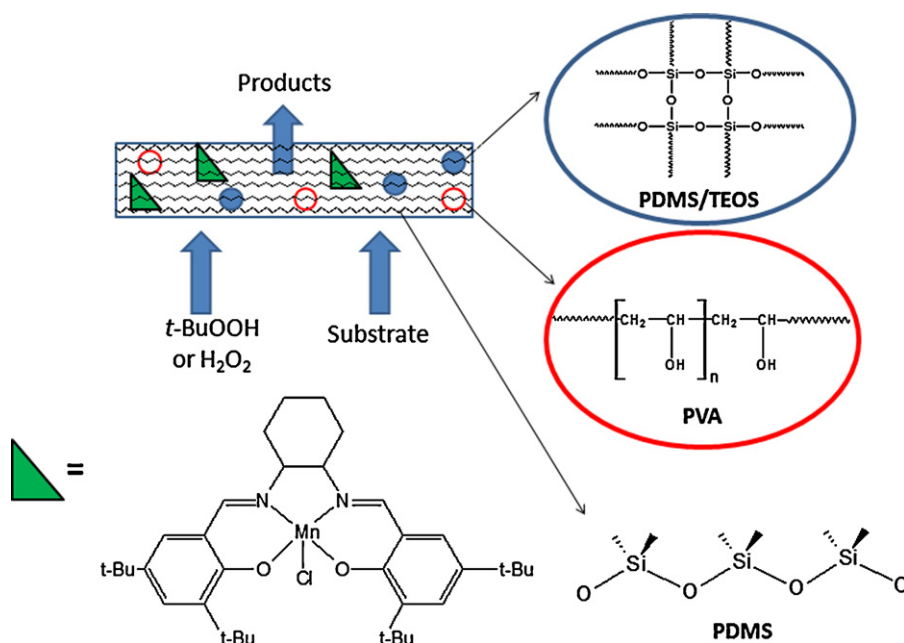


Fig. 2. Schematic representation of substrate (cyclooctene or styrene) epoxidations with a Mn(salen) complex encapsulated in a polymeric PDMS/PVA-semi-IPN (blue circles (full circles) represent the crosslinking of silanol-terminated PDMS with TEOS, and red circles (empty circles) represent the PVA polymer). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

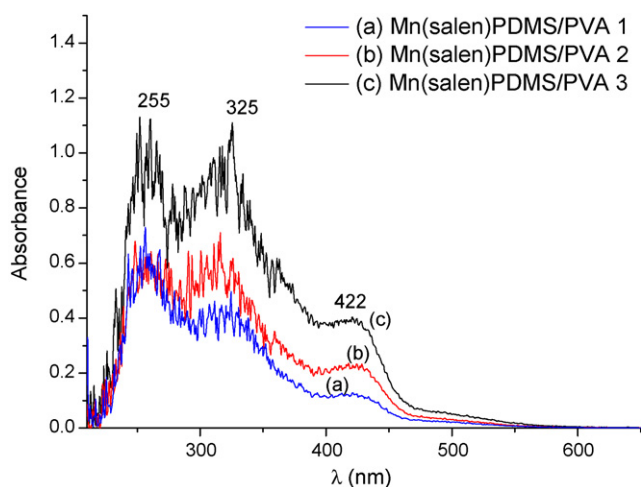


Fig. 3. UV-vis spectra of Mn(salen)PDMS/PVA 1 (a), 2 (b), and 3 (c). The membrane without Mn(salen) was used as reference.

PDMS/PVA 01 semi-IPN. The morphology is characterized by the segregation of PVA chains in the PDMS matrix, forming circular dispersed domains from ~ 1 to $30\ \mu\text{m}$ in diameter. The driving force for segregation of the dispersed PVA domains is the different characteristics between the polar PVA and non-polar PDMS network. Such domains are uniformly distributed in the PDMS matrix. The same morphologies were observed for all the PVA compositions (not shown).

Sorption measurements to evaluate the polarity of the prepared membranes were performed using the substrates (cyclooctene and styrene) and the oxidants ($t\text{-BuOOH}$ and H_2O_2) investigated in this study. After the membrane had been immersed in the substance for 24 h, its mass gain was assessed. The results of these experiments are presented in Table 1.

The data depicted in Table 1 indicate that the polarity of the PDMS/PVA membrane is controlled by the relative ratio between the two constituents. The membrane Mn(salen)PDMS/PVA 1 is typically hydrophobic, with higher affinity for the apolar substrates (styrene and cyclooctene) and lower affinity for the polar oxidants ($t\text{-BuOOH}$ and H_2O_2). Addition of a larger amount of PVA to the PDMS network (membranes 2 and 3) leads to a significant increase in the sorption values obtained for H_2O_2 and, to a lesser extent, for $t\text{-BuOOH}$, as a result of enhanced membrane polarity. In contrast, increasing membrane polarity causes a reduction in membrane swelling in the case of the apolar substrates. In other words, the larger the PVA concentration in the polymeric membrane, the lower values of organic substrate sorption in the material. These results will reflect on the catalytic profile obtained in oxidation reactions catalyzed by these systems, as discussed below.

3.2. Epoxidation reactions

The research on catalytic polymeric membrane has been focused on a variety of reactions such as cyclohexene and styrene epoxidation [36], cyclohexane and $n\text{-dodecane}$ oxidation [39,43,45], $\alpha\text{-pinene}$ hydration [56], methylacetoacetate hydrogenation [57], alcohols photooxidation [58], and secondary amines and sulfides oxidations [59].

In the catalytic system studied in this work we have employed membranes that act as a barrier between two immiscible phases: the organic phase consisting of the substrate (cyclooctene or styrene) and the aqueous phase containing the oxidant ($t\text{-BuOOH}$ or H_2O_2 30%), thereby dismissing the use of solvents and phase-transfer agents (see Fig. 1). This new approach, in association with the sorption properties of the polymer, can drastically influence the catalytic results [38].

The catalytic oxidation results were measured in terms of turnover frequencies (Tables 2 and 3). The oxidation products were analyzed in both the aqueous and organic phases. The distribution

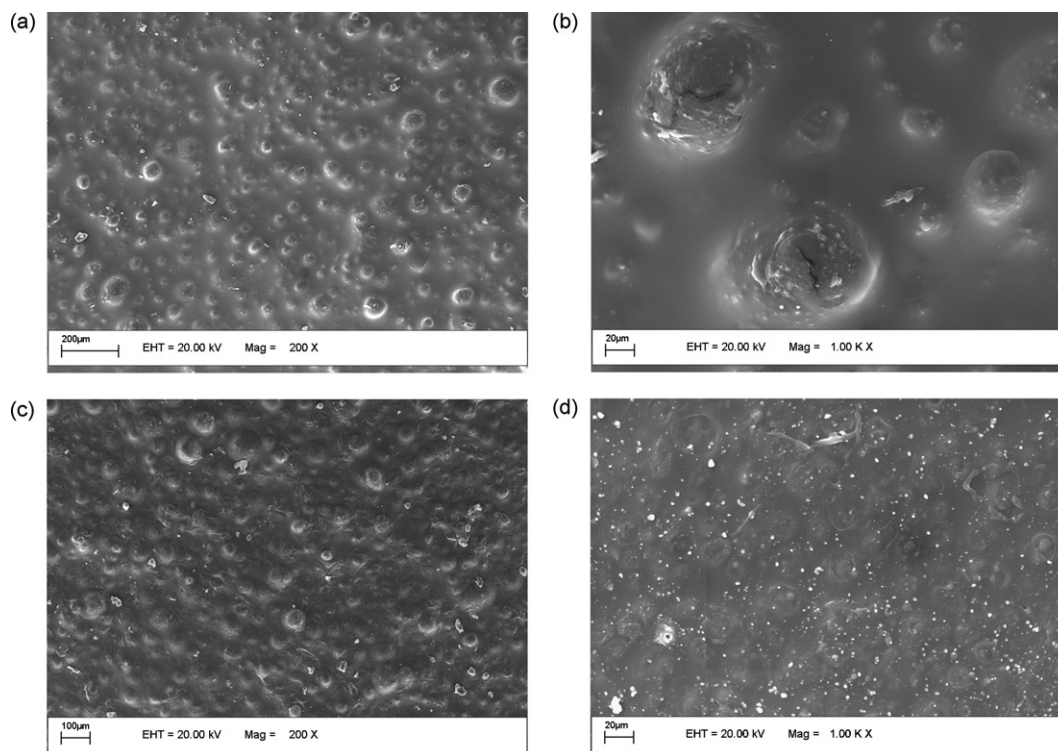


Fig. 4. Cryogenic surface fracture micrographs of the polymeric membrane PDMS/PVA (A) and (B) without catalyst at magnifications 200 \times and 1000 \times , respectively; (C) with occluded Mn(salen) at magnifications 200 \times ; (D) with occluded Mn(salen), after the catalytic reaction, at magnifications 1000 \times .

Table 1

Sorption measurements for the substrates and oxidants in the polymeric membrane Mn(salen)PDMS/PVA 1–3, after 24 h.

Entry	Substrates/oxidants	Sorption in Mn(salen)PDMS–10% PVA 1 (mmol/g)	Sorption in Mn(salen)PDMS–15% PVA 2 (mmol/g)	Sorption in Mn(salen)PDMS–20% PVA 3 (mmol/g)
1	Styrene	8.96	6.20	5.27
2	Cyclooctene	13.20	10.30	8.41
3	t-BuOOH	4.00	4.30	4.62
4	H ₂ O ₂	2.30	9.70	14.9

of the hydrocarbon oxidation products depended on their affinity for the organic and aqueous phases. They could be recovered in both phases, with higher concentrations being found in the former phase.

Results from Tables 2 and 3 reveal that the catalytic efficiency of these systems depends essentially on the polarity of the membrane where the catalyst is occluded. This is because the polarity of the membrane controls the sorption properties of the polymeric matrix. The oxidant t-BuOOH has a hydrophobic character, and its sorption is favored in the case of the membrane Mn(salen)PDMS/PVA 1, which contains a lower amount of the more polar polymer (PVA) (Tables 2 and 3, entries 1 and 2). As a result, the catalytic efficiency of the system Mn(salen)PDMS/PVA 1 + t-BuOOH is higher if compared with that obtained for Mn(salen)PDMS/PVA 1 + H₂O₂, since t-BuOOH is less polar. On the other hand, the membrane Mn(salen)PDMS/PVA 3, which contains a higher PVA (polar polymer) ratio, is more catalytically efficient in the presence of the polar oxidant H₂O₂ (Tables 2 and 3, entries 5 and 6).

The use of hydrogen peroxide as oxidant is advantageous for various reasons: it is inexpensive, gives water as the sole product, and is more readily available than t-BuOOH. For all these reasons, hydrogen peroxide is considered a clean oxidant that is potentially applicable in metalloporphyrin- and salen complex-catalyzed oxidations. However, catalyst activity in the presence of this oxidant is limited due to the tendency of H₂O₂ to decompose into H₂O and O₂, a reaction catalyzed by metal complexes, similar to the reaction occurring in the presence of the enzyme catalase *in vivo*. Furthermore, peroxides can undergo homolytic cleavage of the O–O bond, thereby triggering radical reactions that destroy the catalyst and/or support, thus leading to low product yields [60]. Therefore, the high turnover frequency values achieved with the membrane Mn(salen)PDMS/PVA 3, TOF 138 h^{−1} and TOF 80 h^{−1} for the substrates styrene and cyclooctene, respectively (Tables 2 and 3, entry 5), are considered excellent catalytic results.

These results also demonstrate the positive effects of adding the polar polymer PVA to the Mn(salen)PDMS membrane. Previous systems using the latter membrane in the absence of PVA were not able to promote styrene or cyclooctene oxidation by hydrogen perox-

ide due to the inability of the membrane to sorb this polar oxidant [31] (Tables 2 and 3, entry 7). Results from alkene oxidation using the oxidant t-BuOOH and the membrane Mn(salen)PDMS were also inferior to those obtained with the more polar membranes (containing PVA) used in this work (Tables 2 and 3, entries 8 vs 2, 4, 6).

When peroxide oxidants (t-BuOOH and H₂O₂) are used, two mechanisms for oxygen activation are possible: one involves the homolytic cleavage of the O–O peroxide bond, with RO• as the active species, and results in low selectivity; the other involves the heterolytic cleavage of the O–O bond, with formation of the Mn^V(O)salen species, responsible for the epoxidation [60,61]. In other words, the oxidation products indicate the main mechanism through which the oxidation reaction proceeds. In the present work, cyclooctene oxidation reactions furnished cyclooctenoxide as the sole product, while styrene oxidation gave styrene oxide as the main oxidation product in reactions using t-BuOOH as oxidant. On the other hand, H₂O₂ led to higher selectivity for benzaldehyde, suggesting contribution from radical mechanisms. When the reaction was carried out under argon, the benzaldehyde turnover frequency was significantly reduced, and the selectivity toward styrene oxide increased (Table 2, entries 9–11). This result gives evidence that alkyl radicals are formed in the reaction, and that they could be trapped by O₂.

Higher PVA ratios in the membrane resulted in larger styrene oxide production and a consequent decrease in benzaldehyde formation in reactions carried out with the oxidant H₂O₂ (Table 2, entries 1, 3, and 5). This shows that, besides increasing H₂O₂ sorption, larger membrane polarity leads to higher selectivity for epoxide formation, probably by favoring the heterolytic cleavage of the peroxide O–O bond [62].

Table 2 evidences formation of phenylacetaldehyde as by-product. Its production is related to the reactivity of the intermediate species (activated complex); i.e., the lower reactivity and the longer lifetime of the intermediate species increase the probability of hydrogen rearrangement, which competes with styrene oxide formation [62–64]. Inside the membrane, the reaction depends on the restrict diffusion of the substrate and oxidant, which favors rearrangement of the intermediate species.

Table 2Results obtained for styrene oxidation reactions by t-BuOOH and H₂O₂ catalyzed by Mn(salen)PDMS/PVA with different degrees of PVA and Mn(salen)PDMS (without PVA).

Entry	Catalyst	Oxidant	TOF styrene oxide	TOF benzaldehyde	TOF phenylacetaldehyde	TOF total
1	Mn(salen)PDMS/PVA 1	H ₂ O ₂	21	79	ND	100
2	Mn(salen)PDMS/PVA 1	t-BuOOH	115	27	5	147
3	Mn(salen)PDMS/PVA 2	H ₂ O ₂	29	76	7	112
4	Mn(salen)PDMS/PVA 2	t-BuOOH	87	38	4	129
5	Mn(salen)PDMS/PVA 3	H ₂ O ₂	43	68	27	138
6	Mn(salen)PDMS/PVA 3	t-BuOOH	79	35	2	116
7	Mn(salen)PDMS ^a	H ₂ O ₂	ND	ND	ND	ND
8	Mn(salen)PDMS ^a	t-BuOOH	102	7	ND	109
9	Mn(salen)PDMS/PVA 1 ^b	H ₂ O ₂	45	32	ND	77
10	Mn(salen)PDMS/PVA 2 ^b	H ₂ O ₂	53	27	12	92
11	Mn(salen)PDMS/PVA 3 ^b	H ₂ O ₂	67	23	28	118
12	Mn(salen)PDMS/PVA 1 ^b	t-BuOOH	117	24	3	144

Mn(salen)PDMS/PVA 1: 10% PVA; Mn(salen)PDMS/PVA 2: 15% PVA; Mn(salen)PDMS/PVA 3: 20% PVA. ND: not detected.

^a Mn(salen)PDMS: without PVA [31].^b Reaction is carried out under argon.

Table 3
Results obtained for cyclooctene oxidation reactions by t-BuOOH and H₂O₂ catalyzed by Mn(salen)PDMS/PVA with different degrees of PVA and Mn(salen)PDMS (without PVA).

Entry	Catalyst	Oxidant	TOF cyclooctene oxide	TOF total
1	Mn(salen)PDMS/PVA 1	H ₂ O ₂	46	46
2	Mn(salen)PDMS/PVA 1	t-BuOOH	72	72
3	Mn(salen)PDMS/PVA 2	H ₂ O ₂	59	59
4	Mn(salen)PDMS/PVA 2	t-BuOOH	71	71
5	Mn(salen)PDMS/PVA 3	H ₂ O ₂	80	80
6	Mn(salen)PDMS/PVA 3	t-BuOOH	69	69
7	Mn(salen)PDMS ^a	H ₂ O ₂	ND	ND
8	Mn(salen)PDMS ^a	t-BuOOH	12	12

Mn(salen)PDMS/PVA 1: 10% PVA; Mn(salen)PDMS/PVA 2: 15% PVA; Mn(salen)PDMS/PVA 3: 20% PVA. ND: not detected.

^a Mn(salen)PDMS: without PVA [31].**Table 4**
Results obtained for cyclooctene oxidation by t-BuOOH and H₂O₂ catalyzed by Mn(salen)PDMS/PVA and Mn(salen)PDMS membranes in two different systems: triphasic systems (membrane as interface) and biphasic system (acetonitrile as solvent).

Entry	Catalyst	Oxidant	TOF cyclooctene oxide—membrane at the interface ^a	TOF cyclooctene oxide—biphasic system ^b
1	Mn(salen)PDMS/PVA 1	H ₂ O ₂	46	31
2	Mn(salen)PDMS/PVA 1	t-BuOOH	72	67
3	Mn(salen)PDMS/PVA 2	H ₂ O ₂	59	36
4	Mn(salen)PDMS/PVA 2	t-BuOOH	71	55
5	Mn(salen)PDMS/PVA 3	H ₂ O ₂	80	58
6	Mn(salen)PDMS/PVA 3	t-BuOOH	69	54
7	Mn(salen)PDMS ^c	H ₂ O ₂	ND	ND
8	Mn(salen)PDMS ^c	t-BuOOH	12	8

Mn(salen)PDMS/PVA 1: 10% PVA; Mn(salen)PDMS/PVA 2: 15% PVA; Mn(salen)PDMS/PVA 3: 20% PVA. ND: not detected.

^a Reaction condition: 50 mg of membrane, containing 1.6×10^{-8} mol of the Mn(salen), oxidant (t-BuOOH or H₂O₂: 7.8×10^{-4} mol), substrate (cyclooctene: 6.5×10^{-3} mol) solvent-free.^b Reaction condition: 50 mg of membrane containing 1.6×10^{-8} mol of the Mn(salen), oxidant (t-BuOOH or H₂O₂: 7.8×10^{-4} mol), substrate (cyclooctene: 1×10^{-3} mol) using acetonitrile (3 mL).^c Mn(salen)PDMS: without PVA [31].

The catalytic activities of the Mn(salen)PDMS/PVA 1–3 membranes were also evaluated by placing them in two different systems, namely a triphasic system, where the membranes are positioned exactly in the interface of the aqueous oxidant and organic substrate because of their intermediate density, and a biphasic system, with the membranes being added to a solution of the oxidant and substrate in acetonitrile, the other conditions being the same. The results are shown in Table 4.

It can be observed that in a solvent-free triphasic reactor, where the membrane is at the interface, clearly enhanced reaction TOFs were achieved compared with the biphasic system. The difference in the catalytic activities of Jacobsen catalyst in different systems can be explained on the basis of the sorption and diffusion properties of the various reactants and products into the poly(dimethylsiloxane) polymer. In the biphasic system the solvent inevitably decreases reagent concentrations, while in triphasic one the pure substrate and oxidant are sorbed by the membrane where the catalyst is located. This concept of using PDMS membrane at the interface has also been studied by other authors for many catalysts, with the best results being obtained in reactions that involve immiscible reagent phases [65,66].

In order to evaluate the possible recycling of the Mn-containing membrane, the latter was thoroughly washed with CH₃CN under vigorous stirring and then reused for a new set of epoxidation experiments. Unfortunately, the catalytic activity of the recycled membrane was much lower than that of the fresh one. This is most likely due to blockage of the active sites by adsorption onto the membrane surface of reactants that had not been completely removed during the membrane washing procedure, instead of metal leaching. Indeed, eventual leaching from the membrane of the supported Mn(salen) complex in the presence of different solvents was screened by UV–vis spectroscopy. Slight Mn leaching was observed in the case of apolar solvents (such as CH₂Cl₂), whereas this process did not occur in the presence of a polar one (e.g.,

CH₃CN) due to the lower swelling of the membrane in this kind of solvent. In order to investigate the possible involvement of homogeneous Mn-species in the catalysis, the following experiment was developed: Mn(salen)PDMS/PVA 1 was mixed with t-BuOOH under typical reaction conditions. After 1 h of intensive stirring, the catalytic membrane was removed, and cyclooctene was added into this solution. After additional stirring for 5 h, the reaction solution was analyzed by gas chromatography as usual. No traces of epoxide were observed, thus excluding the hypothesis of involvement of a homogeneous route in the catalysis, fully supporting the heterogeneous process.

4. Conclusions

The hybrid membranes PDMS/PVA were evaluated in a triphasic system, where the membrane is located in the interface between the apolar (organic substrate) and aqueous (containing the oxidant) phases. The catalytic results were excellent, with turnover frequencies in the order of 138 h^{-1} in the case of hydrogen peroxide and up to 147 h^{-1} with t-BuOOH. These membranes are promising candidates for the development of reactors with separation between substrate and oxidant by the polymeric membrane. This new triphasic system containing a cheap and easily available catalyst allowed substrate oxidation and easy product separation using “green” oxidants. The results show that it is possible to modulate the polarity of the polymeric membrane, so that the desired reactants can be more promptly sorbed. This shall render catalysis more selective toward the substrate and oxidant of interest.

This study was carried out on laboratory scale and revealed that this system would have potential industrial applications. However, the conditions for any commercial application should be tested, since increasing the loading of the catalyst could make its leaching easier. In addition, the reaction is limited by the dimension of the membrane, since the mechanism of this process is based just on the

diffusion of solvent (substrate) and oxidant into the membrane. No pressure has been applied. Therefore, based on the glass reactor designed for these experiments, it seems that it would be feasible for batch reactions on an industrial scale.

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References

- [1] R.A. Sheldon, I. Arends, U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, Germany, 2007, pp. 1–434.
- [2] R.A. Sheldon, in: M.P.C. Weijnen, A.A.H. Drinkenburg (Eds.), *Precision Process Technology*, Kluwer, Dordrecht, 1993, pp. 125–138.
- [3] R.A. Sheldon, *Top. Curr. Chem.* 164 (1993) 21–43.
- [4] R.A. Sheldon, *J. Mol. Catal. A: Chem.* 107 (1996) 75–83.
- [5] R.A. Sheldon, *Chem. Commun.* 29 (2008) 3352–3365.
- [6] W.F. Hoelderich, F. Kollmer, *Pure Appl. Chem.* 72 (2000) 1273–1287.
- [7] V.K. Sharma, F. Kazama, H. Jiangyong, A.K. Ray, *J. Wat. Health* (2005) 45–57.
- [8] J.H. Clark, *Pure Appl. Chem.* 73 (2001) 103–111.
- [9] E.N. Jacobsen, W. Zhang, M.L. Güler, *J. Am. Chem. Soc.* 113 (1991) 6703–6704.
- [10] R. Irie, K. Noda, Y. Ito, T. Katsuki, *Tetrahedron Lett.* 32 (1991) 1055–1058.
- [11] B.D. Brandes, E.N. Jacobsen, *Tetrahedron Lett.* 36 (1995) 5123–5126.
- [12] M. Palucki, G.J. McCormick, E.N. Jacobsen, *Tetrahedron Lett.* 36 (1995) 5457–5460.
- [13] H. Sasaki, R. Irie, T. Hamada, K. Suzuki, T. Katsuki, *Tetrahedron* 50 (1994) 11827–11838.
- [14] N. Hosoya, A. Hatayama, R. Irie, H. Sasaki, T. Katsuki, *Tetrahedron* 50 (1994) 4311–4322.
- [15] B. Gong, X. Fu, J. Chen, Y. Li, X. Zou, X. Tu, P. Ding, L. Ma, *J. Catal.* 262 (2009) 9–17.
- [16] K. Yu, Z. Gu, R. Ji, L. Lou, S. Liu, *Tetrahedron* 65 (2009) 305–311.
- [17] K.C. Gupta, A.K. Sutar, C.C. Lin, *Coord. Chem. Rev.* 253 (2009) 1926–1946.
- [18] A. Stamatis, P. Doutsis, C. Vartzouma, K.C. Christoforidis, Y. Deligiannakis, M. Louloudi, *J. Mol. Catal. A: Gen.* 297 (2009) 44–53.
- [19] M. Bagherzadeh, L. Tahsini, R. Latifi, *Catal. Commun.* 9 (2008) 1600–1606.
- [20] L.D. Pinto, J. Dupont, R.F. de Souza, K. Bernardo-Gusmao, *Catal. Commun.* 9 (2008) 135–139.
- [21] P. Das, I. Kuzniarska-Biernacka, A.R. Silva, A.P. Carvalho, J. Pires, C. Freire, *J. Mol. Catal. A: Chem.* 248 (2006) 135–143.
- [22] B. Bahramian, V. Mirkhan, M. Moghadam, S. Tangestaninejad, *Catal. Commun.* 7 (2006) 289–296.
- [23] H.D. Zhang, Y.M. Wang, L. Zhang, G. Gerritsen, H.C.L. Abbenhuis, R.A. van Santen, C. Li, *J. Catal.* 256 (2008) 226–236.
- [24] A.R. Silva, K. Wilson, J.H. Clark, C. Freire, *Micropor. Mesopor. Mater.* 91 (2006) 128–138.
- [25] R.J. Correa, G.C. Salomao, M.H.N. Olsen, L. Cardozo, V. Drago, C. Fernandes, O.A.C. Antunes, *Appl. Catal. A: Gen.* 336 (2008) 35–39.
- [26] V. Mirkhani, M. Moghadam, S. Tangestaninejad, B. Bahramian, A. Mallekpoor-Shalamzari, *Appl. Catal. A: Gen.* 321 (2007) 49–57.
- [27] M. Silva, C. Freire, B. de Castro, J.L. Figueiredo, *J. Mol. Catal. A: Chem.* 258 (2006) 327–333.
- [28] D. Srinivas, S. Sivasanker, *Catal. Surv. Asia* 7 (2003) 121–132.
- [29] T. Joseph, D. Srinivas, C.S. Gopinath, S.B. Halligudi, *Catal. Lett.* 83 (2002) 209–214.
- [30] B. Fan, H. Li, W. Fan, C. Jin, R. Li, *Appl. Catal. A: Gen.* 340 (2008) 67–75.
- [31] D.F.C. Guedes, T.C.O. Mac Leod, M.C.A.F. Gotardo, M.A. Schiavon, I.V.P. Yoshida, K.J. Ciuffi, M.D. Assis, *Appl. Catal. A: Gen.* 296 (2005) 120–127.
- [32] T.C.O. Mac Leod, V.P. Barros, A.L. Faria, M.A. Schiavon, I.V.P. Yoshida, M.E.C. Queiroz, M.D. Assis, *J. Mol. Catal. A: Chem.* 273 (2007) 259–264.
- [33] T.C.O. Mac Leod, M.V. Kirillova, A.J.L. Pombeiro, M.A. Schiavon, M.D. Assis, *Appl. Catal. A: Gen.* 372 (2010) 191–198.
- [34] D. Disalvo, D.B. Dellinger, J.W. Gohdes, *React. Funct. Polym.* 53 (2002) 103.
- [35] L. Canali, E. Cowan, H. Deleuze, C.L. Gibson, D.C. Sherrington, *J. Chem. Soc. Perkin Trans. I* (2000) 2055–2066.
- [36] P.P. Knops-Gerrits, I.F.J. Vankelecom, E. Beatse, P.A. Jacobs, *Catal. Today* 32 (1996) 63–70.
- [37] D.A. Annis, E.N. Jacobsen, *J. Am. Chem. Soc.* 121 (1999) 4147–4154.
- [38] I.F.J. Vankelecom, R.F. Parton, M.J.A. Casselman, J.B. Uytterhoeven, P.A. Jacobs, *J. Catal.* 163 (1996) 457–464.
- [39] G. Langhendries, G.V. Baron, I.F.J. Vankelecom, R.F. Parton, P.A. Jacobs, *Catal. Today* 56 (2000) 131–135.
- [40] I.F.J. Vankelecom, P.A. Jacobs, *Catal. Today* 56 (2000) 147–157.
- [41] I.F.J. Vankelecom, K. Vercruysse, N. Moens, R.F. Parton, J.S. Reddy, P.A. Jacobs, *Chem. Commun.* (1997) 137–138.
- [42] S.S. Ozdemir, M.G. Buonomenna, E. Drioli, *Appl. Catal. A: Gen.* 307 (2006) 167–183.
- [43] M.C.A. Gotardo, A.A. Guedes, M.A. Schiavon, N.M. José, I.V.P. Yoshida, M.D. Assis, *J. Mol. Catal. A: Chem.* 229 (2005) 137–143.
- [44] R.F. Parton, I.F.J. Vankelecom, D. Tas, B.M. Janssen, P.P. Knops-Gerrits, P.A. Jacobs, *J. Mol. Catal. A: Chem.* 113 (1996) 283–292.
- [45] A. Wolfson, S. Geresh, M. Gottlieb, M. Herskowitz, *Tetrahedron: Asymm.* 13 (2002) 465–468.
- [46] S.Y. Ren, Z.F. Xie, X.P. Xie, G.F. Qin, J. Wang, *Progr. Chem.* 21 (2009) 663–671.
- [47] M.G. Buonomenna, E. Drioli, *Appl. Catal. B: Environ.* 79 (2008) 35–42.
- [48] S. Mukherjee, S. Samanta, A. Bhaumik, B.C. Ray, *Appl. Catal. B: Environ.* 68 (2006) 12–20.
- [49] H. Einaga, S. Futamura, *Appl. Catal. B: Environ.* 60 (2005) 49–55.
- [50] S. Bawaked, N.F. Dummer, N. Dimitratos, D. Bethell, Q. He, C.J. Kiely, G.J. Hutchings, *Green Chem.* 11 (2009) 1037–1044.
- [51] R.S. Marques, T.C.O. Mac Leod, I.V.P. Yoshida, V. Mano, M.D. Assis, M.A. Schiavon, *J. Appl. Pol. Sci.* 115 (2010) 158–166.
- [52] X. Hao, M. Pritzker, X. Feng, *J. Membr. Sci.* 335 (2009) 96–102.
- [53] B. Ortiz, S. Park, *Bull. Korean Chem. Soc.* 21 (4) (2000) 405–411.
- [54] P.E.F. Neys, I.F.J. Vankelecom, M. L'abbe, R.F. Parton, E. Cenlemans, W. Dehaen, G. L'abbe, P.A. Jacobs, *J. Mol. Catal. A: Chem.* 134 (1998) 209–214.
- [55] P.E.F. Neys, A. Severeyns, I.F.J. Vankelecom, E. Ceulemans, W. Dehaen, P.A. Jacobs, *J. Mol. Catal. A: Chem.* 144 (1999) 373–377.
- [56] J. Vital, A.M. Ramos, I.F. Silva, H. Valente, J.E. Castanheiro, *Catal. Today* 56 (2000) 167.
- [57] I.F.J. Vankelecom, N.M.F. Moens, K.A.L. Vercruysse, R.F. Parton, P.A. Jacobs, in: H.U. Blaser, A. Baiker, R. Prins (Eds.), *Heterogeneous Catalysis and Fine Chemicals*, IV, Elsevier, Amsterdam, 1997, p. 437.
- [58] M. Bonchio, M. Carraro, G. Scorrano, E. Fontananova, E. Drioli, *Adv. Synth. Catal.* 345 (2003) 119.
- [59] M.G. Buonomenna, E. Drioli, R. Bertoncello, L. Milanese, P. Scrimin, G. Licini, *J. Catal.* 238 (2006) 221.
- [60] J.T. Groves, *J. Inorg. Biochem.* 100 (2006) 434–447.
- [61] B.S. Lane, K. Burgess, *Chem. Rev.* 103 (2003) 2457–2473.
- [62] T.C.O. Mac Leod, D.F.C. Guedes, M.R. Lelo, R.A. Rocha, B.L. Caetano, K.J. Ciuffi, M.D. Assis, *J. Mol. Catal. A: Chem.* 259 (2006) 319–327.
- [63] W. Nam, I. Kim, M.H. Lim, H.J. Choi, J.S. Lee, H.G. Jang, *Chem. Eur. J.* 8 (2002) 2067–2071.
- [64] A.A. Guedes, A.C.M.A. Santos, M.D. Assis, *Kinet. Catal.* 47 (2006) 555–563.
- [65] J.A. Martens, D.E. De Vos, C.E.A. Kirschhock, P.P. Pescarmona, B. Sels, I.F.J. Vankelecom, *Top. Catal.* 52 (2009) 1119–1130.
- [66] I.F.J. Vankelecom, *Chem. Rev.* 102 (2002) 3779–3810.